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# (54) PRODUCT AND METHOD FOR CLEANING TITANIUM SURFACES

(57) The cleaning product includes, separately, (A) a descaling substance consisting of a mixture of nitric acid and hydrofluoric acid, a thickener, a surfactant, an indicator, water and, optionally, a propellant; and (B) a fixative composition that consists of a base, a thickener,

a surfactant and a propellant. This cleaning product is useful for cleaning titanium surfaces such as titanium facades and panels.

#### Description

#### AREA OF THE INVENTION

[0001] The invention concerns a cleaning product to clean titanium surfaces and its application in a procedure to clean titanium surfaces such as titanium facades and panels.

# **BACKGROUND OF THE INVENTION**

[0002] The excellent resistance of titanium and its alloys to corrosion is due to the formation of a protective film of oxides, which is continuous, stable and adheres strongly to the surface. Owing to the high affinity of titanium for oxygen, this film of oxides forms spontaneously as soon as a recent cut of the material is exposed to the atmosphere.

[0003] The nature, composition and thickness of the layer of protective oxides formed on the surface of the titanium depend on environmental conditions. In most aqueous environments, the oxide formed is TiO2, although also a mixture of TiO2, Ti2O3 and TiO can also be formed. The naturally formed oxide films reach thicknesses of around 10 nm, which are not visible with the naked eye.

[0004] Some factors can alter the characteristics and composition of the TiO2 layer, including the temperature or affinity of titanium for certain gases. Also, the presence of contamination or dirt on the metal surface can produce discontinuities in the surface that can give rise to severe localized corrosion processes. In the case of titanium panels used in construction and exposed to aggressive environmental, industrial and urban atmospheres, this type of phenomenon, which alters the surface characteristics of the panels and their composition, has been observed.

[0005] Cleaning and surface passivation methods used in normal conditions to eliminate this type of oxide and surface contamination require immersion processes that use different types of solutions. These include acid pickling, electropolishing or mechanical processes. These methods are not viable in panels used for construction purposes owing to their high cost and because they can alter the surface characteristics of the original panels.

[0006] There is, therefore, the need for a new method to clean surfaces containing titanium, such as the titanium panels used in construction, that can help to overcome all or most of the problems described here.

#### SUMMARY OF THE INVENTION

[0007] The invention, in general, deals with the problem of providing a method to clean titanium surfaces such as the titanium panels used to build facades.

[0008] The solution provided by the invention is based on the development of a cleaning product that includes, separately, (i) a descaling substance, which contains an active agent that acts on the metal surface, composed of a mixture of inorganic acids, and (ii) a fixative, which inhibits and neutralizes the action of the descaling substance, and also in the application of this cleaning product to clean titanium surfaces.

[0009] The application of the cleaning product and the cleaning method provided by this invention permit easy and precise cleaning of the titanium surface without damaging it.

[0010] This cleaning product and its application to clean titanium surfaces are both the objectives of this invention.

# **DETAILLED DESCRIPTION OF THE INVENTION**

[0011] The invention provides a cleaning product, useful for cleaning titanium surfaces, that includes, separately, (A) a descaling or cleaning substance, from hereon called the descaling substance, which contains an active agent that acts on the metal surface, which is composed of a mixture of inorganic acids, and, (B) a fixative or neutralizer, from hereon referred to as the fixative, which inhibits and neutralizes the action of the descaling substance.

[0012] More specifically, the cleaning product of the invention corresponds, separately, to:

A) a descaling substance comprised of:

A.1) a mixture of nitric acid and hydrofluoric acid;

A.2) a thickening agent;

A.3) a surfactant;

A.4) an indicator;

A.5) water; and, optionally,

A.6) a propellant; and

B) a fixative substance that contains:

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- B.1) an alkaline aqueous solution;
- B.2) a thickener:
- B.3) a surfactant;
- B.4) water; and

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B.5) a propellant.

# A. Composition of descaling substance

[0013] The composition of the descaling substance consists of water, an active agent and auxiliary agents (thickener, surfactant and indicator), as well as a propellant.

[0014] The active agent is comprised of a mixture of nitric and hydrofluoric acid, and acts on the metal surface (Ti), providing the chemical reaction responsible for eliminating the contamination, impurities and oxides. Beneficially, the active agent also has a protective effect to prevent progression of the cleaning chemical reaction on the metal substrate. The active agent, usually added in the form of an aqueous solution, is present in the descaling substance in a concentration ranging from 1 to 20% in weight relative to the total descaling composition. In a specific application, this active agent consists of a mixture of nitric acid and hydrofluoric acid that contains between 1% and 10% in weight of nitric acid compared to the total descaling composition and between 0.1% and 1% in weight of hydrofluoric acid relative to the total descaling composition, and the weight ratio of nitric acid: hydrofluoric acid is 10:1.

[0015] The thickener is introduced in the descaling substance as a stabilizer, also giving it viscosity and selected rheological characteristics. As a thickening agent, a water-soluble organic pseudoplastic thickener can be used, for example, of cellulotic type or a natural gum, for example xanthane gum. The thickening agent can be present in the descaling substance in a concentration ranging from 0.1% to 1% in weight relative to the total descaling composition.

[0016] The surfactant alters the surface tension of the descaling substance, favoring the formation of foam, stabilization of this substance and dispersion of its components. Potential surfactants include ionic ones (anionic or cationic), in concentrations ranging from 0.1 to 1% in weight compared to the total descaling composition. In one specific application this surfactant is sodium dodecyl sulphate.

[0017] The indicator is introduced in the descaling substance to indicate, by a color change, the time of neutralization of the descaling substance applied on the metallic surface by the fixative substance. The indicator is present in the descaling substance at a concentration less than 0.1% in weight relative to the total weight of descaling substance. In one application the indicator used is phenolphthalein.

[0018] The water present in the descaling substance can come from the active agent (if the acids present are supplied in aqueous solution) and/or from the auxiliary agents (if these are provided dissolved or suspended in water) and/or from water added to make up the descaling solution.

[0019] The descaling substance can take one of several different forms, for example, it can be a foam, gel or a spray gel. Depending on its form of preparation and packaging, the descaling substance may or may not contain a propellant.

[0020] The propellant is a substance that provides the packaged descaling substance with a high internal pressure that results in its forced ejection onto the metallic surface to be cleaned. The propellant can be a liquated or compressed gas.

[0021] Liquated gases are substances that are liquid at ambient temperature, due to the effect of pressure, and that become gaseous at atmospheric pressure. At a specific temperature, the high working pressure is constant and equals the vapor pressure of the liquated propellant. Vaporization of the propellant into the atmosphere favors spray formation or conversion into fine droplets of the non-volatile compounds in solution favoring the formation of microfoams. Examples of liquated gases include hydrocarbons and hydrofluorocarbons (HFC), which can be used at a concentration ranging from 5% to 20% in weight relative to the total descaling composition. In one specific application, the propellant is hydrofluorocarbon identified as HFC 134a (1,1,1,2-tetrafluoroethane).

[0022] Compressed gases are substances injected at appropriate pressures that maintain the excess pressure on the surface of the descaling substance in the container, forcing this to the exterior in the same way as an embolus that acts on the surface of a liquid, especially in the case of insoluble gases. As the contents are discharged, the gas occupies an increasingly larger volume, its initial pressure is reduced and, therefore, the initial working conditions change. Nitrogen, carbon dioxide, nitrous oxide and air can be used in appropriate amounts at the required working pressure.

[0023] As mentioned previously, the preparation and packaging of the descaling compound depends on the form or type of viscous vehicle concerned. As an example, this descaling compound can take the form of:

- a) foam (FD), when the propellant used is a liquated gas;
- b) spray gel (SPD), when the propellant used is a compressed gas; or
- c) gel (GD), when it does not contain propellant.

[0024] The foam and spray gel products are prepared in pressurized containers resistant to acid media, from the following components [active agent, auxiliary agents (in gel form or as an aqueous mixture of thickener, surfactant and indicator), water and gas propellant, in the proportions appropriate to satisfy the percentages defined for the final desired product]. In this case, application of the descaling substance is done, for example, by spraying with a gun, with a maximum interval of 3 hours between filling the container and application of the product, preferably less than 1 hour. [0025] The gel type product is prepared in acid-resistant containers from the following components [active agent, gel or aqueous mixture of auxiliary agents (thickener, surfactant and indicator) and water, in appropriate proportions to satisfy the percentages defined for the final desired product]. In this case, application of the product is done, for example by sponge trowel, with a maximum time interval between filling the container and using the product of 3 hours, and preferably under 1 hour.

# B. Fixative substance

**[0026]** The fixative is comprised of a neutralizing active agent that stops the action of the descaling agent, neutralizing it, some auxiliary agents (thickener and surfactant), water and a propellant.

[0027] The neutralizing active agent inhibits the action of the acid present in the descaling substance when the fixative is applied to the metallic surface thus reducing the likelihood of a too aggressive attack of the acid on the metallic surface, neutralizing the cleaning product and favoring its collection and elimination. As a neutralizing active agent, a base can be used, generally in the form of an aqueous solution, capable of neutralizing the acid present in the descaling substance. As an example, this base can be an alkaline metal hydroxide, for example, sodium hydroxide, in a concentration of between 1% and 20% in weight relative to the total fixative composition, or trisodium phosphate, in a concentration of between 1% and the maximum permitted concentration relative to the fixative.

[0028] The thickener has the same function as mentioned previously relative to the descaling substance. In this case, as a thickening agent, preferentially, inorganic products with a silicate base are used, for example, sepiolite, at a concentration ranging from 1 to 8% in weight relative to the total fixative composition, since this type of thickener can also neutralize the hydrofluoric acid of the descaling substance.

[0029] The surfactant fulfils the same function as that mentioned for the descaling substance. The surfactant present in the fixative can correspond to ionic surfactants (anionic or cationic), that can be the same or different to those used in the descaling substance. The surfactant can be present in the fixative in a concentration ranging from 0.1 to 1% in weight relative to the total fixative composition.

[0030] The water present in the fixative can either come from the neutralizing active agent (if the base is supplied in aqueous solution) and/or from auxiliary agents (in the case that these are supplied dissolved or suspended in water) and/or of water that is incorporated to make up the volume of the fixative.

[0031] The propellant, which can be a liquated gas or a compressed gas, fulfils the same function as that mentioned previously relative to the descaling substance. The propellant present in the fixative compound can be the same as or different to that used in the descaling substance(if this contains propellant). The propellant can be present in the fixative substance in a concentration ranging from 5 to 20% in weight relative to the total fixative composition when the propellant is a liquated gas, for example, a hydrocarbon or a HFC, such as HFC 134a. Alternatively, when the propellant is a compressed gas, for example, nitrogen, carbon dioxide, nitrous oxide or air, this propellant is used, as mentioned previously, in the appropriate quantity at the working temperature required.

[0032] The fixative can take any suitable form of presentation such as foam(FF) when the propellant is a liquated gas or in the form of spray gel (SGF) when the propellant is a compressed gas.

[0033] Both products (foam and spray gel) are kept in pressurized containers resistant to alkaline media, and are composed of the following components [neutralizing active agents, auxiliary agents (in the form of gel or an aqueous mixture of thickener and surfactant) in proportions that satisfy the percentages defined for the final desired product and propellant gas]. Application of the fixative substance is done, for example, by spraying with a gun, with a maximum interval between filling the container and application of the product of 3 hours, but preferably less than 1 hour.

[0034] In one specific application, the invention provides a cleaning product, useful for cleaning titanium surfaces, that also has, separately, the characteristics listed in Table 1.

Table 1

Cleaning Product  A) A descaling compound that contains:		
		A mixture of:
Nitric acid (HNO <sub>3</sub> )	1-10%	
Hydrofluoric acid (HF)	0.1-1%	

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Table 1 (continued)

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Cleaning Product  A) A descaling compound that contains:		
HNO <sub>3</sub> :HF of 10:1		
A thickening agent	0.1-1%	
A surfactant	0.1-1%	
An indicator	<0.1%	
A propellant (liquated gas)	5-20%	
Water (as required for)	100%	
Where the percentages are percentages in weight relative to to and	he total descaling composition;	
B) a fixative substance containing:		
A base	5-15%	
A thickening agent	2-8%	
A surfactant	0.1-1%	
A propellant (liquated gas)	5-20%	
Water (as required for)	100%	
Where the percentages are percentages in weight relative to the	ne total fixative composition.	

[0035] In one specific application of the cleaning product the composition of which is recorded in Table 1, in the descaling composition the active agent is a mixture of 60%HNO<sub>3</sub> and 48% HF, the thickening agent is xanthane gum, the surfactant is sodium dodecyl sulphate, the indicator is phenolphthalein and the propellant (liquated gas) is HFC 134a.

[0036] Similarly, in one specific application of the cleaning product the composition of which is shown in Table 1, in the fixative composition, the base is sodium hydroxide, the thickening agent is sepiolite, the surfactant is sodium dodecyl sulfate and the propellant (liquated gas) is HFC 134a.

[0037] The cleaning product of the invention is useful for cleaning titanium surfaces, especially, titanium building facades. Therefore, the invention provides a method to clean titanium surfaces that consists of using the cleaning product of this invention. More specifically, this method corresponds to the following stages of:

- a) applying the descaling substance of the cleaning product of the invention to the titanium surface to be cleaned and letting it act for a period of time;
- b) applying the fixative composition of the cleaning product of the invention to the titanium surface previously treated with this descaling substance in stage a), and leaving it to act for a period of time;
- c) aspiration of the surfaces previously treated with these descaling and fixative compounds in stages a) and b); and d) rinsing the treated titanium surface after completing stage c).

[0038] Stage a) or the descaling stage consists in applying the descaling substance of the cleaning product of the invention, homogeneously over the whole titanium surface to be cleaned, which is preferentially dry. Where necessary, the titanium surface is dried using instruments that do not cause mechanical damage of the metallic surface. Depending on the form of presentation of the descaling substance, this is administered in one way or another. For example, foam descaling substances (FD) and spray gel descaling substances (SGD) are applied using the appropriate spray gun, while the gel descaling substance (GD) is applied with a sponge trowel taking care not to cause mechanical damage of the metallic surface. After applying the descaling substance to the metallic surface this should be left to act for a period ranging from 15 seconds to 10 minutes before applying the fixative.

[0039] Stage b) or the fixative stage consists in applying the fixative of the cleaning product of the invention to the metallic surface previously treated with the descaling substance in stage a) ensuring that the surface is completely and homogeneously covered. The fixative as foam (FF) and spray gel (SGF) are applied using an appropriate spray gun. After applying the fixative, this is left to act for 30 seconds to 5 minutes before proceeding to the following stage, confirming beforehand that the active neutralizing agent of the fixative substance has neutralized the acid present in the fixative, indicated by the color change of the indicator, or, alternatively, by the use of pH paper indicator strips.

[0040] After the fixation stage, stage c) or the aspiration stage is carried out, in which the previously treated titanium surfaces are aspirated to remove the cleaning products from this previously treated surface. This aspiration is applied

carefully using the appropriate equipment to avoid producing chemical or mechanical damage to the metallic surface. [0041] Finally, after aspiration, step d) or the rinsing is carried out, in which a water jet at a temperature between 5 and 30°C is applied to eliminate the remains of products used in previous stages.

[0042] In one specific application, the titanium surface to be cleaned is a titanium building facade or titanium panels to be used for the construction of facades.

[0043] The following example illustrates application of the invention and should not in any way be considered to limit its scope of application.

# **EXAMPLE 1**

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# Cleaning of a titanium panel

# 1.1 Cleaning product

[0044] Several cleaning products were prepared with formulations included among the compositions recorded in Table 2.

Table 2

Table 2		
Composition of cleaning products of the invention  A) Descaling substance composed of a mixture of:		
HF 48%	0.1-1%	
Weight ratio HNO <sub>3</sub> :HF		
of 10:1		
xanthane gum	0.1-1%	
sodium docedyl sulphate	0.1-1%	
phenolphthalein	<0.1%	
HFC 134a (liquated gas)	5-20%	
Water (as required for)	100%	
Where the percentages are percentages in weight relative to the total	in the descaling compound; an	
B) Fixative containing:		
NaOH	5-15%	
sepiolite	2-8%	
Sodium dodecyl sulphate	0.1-1%	
HFC 134a (liquated gas)	5-20%	
Water (as required for)	100%	
Where the percentages are percentages in weight relative to the to	tal amount of fixative.	

[0045] Both the descaling substance and the fixative are prepared and packaged in foam form by incorporating different compounds in the desired amounts.

# 1.2 Cleaning method

[0046] Titanium panels will be cleaned using cleaning products prepared according to Example 1.1. This will be done by following the protocol described below:

- a) Descaling: the descaling substance of the cleaning product used in each case is applied by spraying the surface of the titanium panels using a spray gun and leaving the product to act for a period ranging from 30 seconds to 3 minutes;
- b) Fixing: the fixative of the cleaning product used in each case is applied to the titanium panels previously treated with the descaling substance using a spray gun and left to act for a period ranging from 30 seconds to 2 minutes;
- c) Aspiration: the products formed and the remains left on the previously treated titanium panels are aspirated with

the help of an aspiration system that is neither chemically or mechanically aggressive; and

d) Rinsing: with water jets at a temperature between 5 and 30°C, to eliminate the remains of products from previous stages.

[0047] The cleaning products tested showed their efficacy at cleaning the treated titanium panels.

#### Claims

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- 1. A cleaning product that is composed, separately, of:
  - A) a descaling substance that consists of:
    - A.1) a mixture of nitric acid and hydrofluoric acid;
    - A.2) a thickener;
    - A.3) a surfactant;
    - A.4) an indicator;
    - A.5) water; and, optionally,
    - A.6) a propellant; and
  - B) a fixative that consists of:
    - B.1) a base;
    - B.2) a thickener;
    - B.3) a surfactant;
    - B.4) water; and
    - B.5) a propellant.
- 2. Cleaning product according to Claim 1, in which this mixture of nitric acid and hydrofluoric acid is present in this descaling substance at a concentration ranging from 1% to 20% in weight relative to the total descaling compound.
  - 3. Cleaning product according to Claim 1, in which the weight ratio of nitric acid: hydrofluoric acid is 10:1.
- Cleaning product according to Claim 1, in which the thickener present in the descaling compound is of watersoluble organic pseudoplastic type.
  - Cleaning product according to Claim 4, in which this water-soluble organic pseudoplastic thickener is selected from cellulotic type thickeners and natural gums.
  - 6. Cleaning product according to Claim 5, in which this thickener is xanthane gum.
  - 7. Cleaning product according to Claim 1, in which this descaling substance contains this thickener in a concentration ranging from 0.1% to 1% in weight relative to the total descaling composition.
  - 8. Cleaning product according to Claim 1, in which the surfactant present in the descaling substance is selected from anionic and cationic surfactants.
  - 9. Cleaning product according to Claim 8, in which this surfactant is sodium dodecyl sulphate.
  - 10. Cleaning product according to Claim 1, in which this descaling substance contains this surfactant in a concentration ranging from 0.1 to 1% in weight relative to the total descaling composition.
  - 11. Cleaning product according to Claim 1, in which this indicator is phenophthalein.

12. Cleaning product according to Claim 1, in which this indicator is present in the descaling substance at a concentration lower than 0.1% in weight relative to the total descaling composition.

- 13. Cleaning product according to Claim 1, in which the propellant present in this descaling composition is a liquated gas selected from among hydrocarbons and hydrofluorocarbons (HFC).
- 14. Cleaning product according to Claim 13, in which the propellant is HFC 134a.

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- 15. Cleaning product according to Claim 1 in which this descaling composition contains a liquated gas as a propellant at a concentration ranging from 5% to 20% in weight relative to the total descaling composition.
- **16.** Cleaning product according to Claim 1, in which this propellant present in the descaling substance is a compressed gas.
  - Cleaning product, according to Claim 16, in which this compressed gas is nitrogen, carbon dioxide, nitrous oxide or air.
- 15 18. Cleaning product according to Claim 1, in which the base, present in this fixative composition is either an alkaline metal hydroxide or trisodium phosphate.
  - 19. Cleaning product according to Claim 18, in which this base present in the fixative composition is sodium hydroxide.
- 20. Cleaning product according to Claim 1 in which this base is present in this fixative at a concentration ranging from 1 to 20% relative to the total fixative composition.
  - 21. Cleaning product according to Claim 1, in which the thickening agent present in the fixative is an inorganic silicate-based thickener.
  - 22. Cleaning product according to Claim 21, in which this thickening agent is sepiolite.
  - 23. Cleaning product according to Claim 1 in which this fixative contains the thickening agent in a concentration ranging from 1% to 8% in weight relative to the total fixative composition.
  - 24. Cleaning product according to Claim 1 in which the surfactant present in the fixative composition is selected from anionic or cationic surfactants.
  - 25. Cleaning product according to Claim 24, in which this surfactant is sodium dodecylsulphate.
  - 26. Cleaning product according to Claim 1, in which this fixative contains this surfactant at a concentration ranging from 0.1% to 1% in weight relative to the total of fixative composition.
- 27. Cleaning product according to Claim 1 in which this propellant present in the fixative is a liquated gas chosen from hydrocarbons or hydrofluorocarbons (HFC).
  - 28. Cleaning product according to Claim 27, in which this propellant is HFC 134a.
- 29. Cleaning product according to Claim 1 in which this fixative contains a liquated gas as a propellant in a concentration ranging from 5% to 20% in weight of the total said fixative.
  - 30. Cleaning product according to Claim 1, in which the propellant present in this fixative is a compressed gas.
- 31. Cleaning product according to Claim 30 in which this compressed gas is nitrogen, carbon dioxide, nitrous oxide or air.
  - 32. Cleaning product according to Claim 1, that includes, separately:
    - A) a descaling substance containing:

A mixture of:	
Nitric acid (HNO <sub>3</sub> )	1-10%

# (continued)

Hydrofluoric acid (HF)	0.1-1%
In which the weight ratio HNO <sub>3</sub> :HF is	10:1
A thickener	0.1-1%
A surfactant	0.1-1%
An indicator	<0.1%
A propellant (liquated gas)	5-20%
Water (as required for)	100%

# B) a fixative containing:

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A base	5-15%
A thickener	2-8%
A surfactant	0.1-1%
A propellant (liquated gas)	5-20%
Water (as required for)	100%
Where the percentages are percentages in weight relative	ve to the total fixative composi-
tion.	,

# 33. Cleaning product according to Claim 32, which includes, separately:

# A) A descaling substance containing:

	A mixture of:	
30	HNO <sub>3</sub> 60%	1-10%
	HF 48%	0.1-1%
	With a weight ratio	
	HNO <sub>3</sub> :HF of 10:1	
35	Xanthane gum	0.1-1%
	Sodium dodecylsulphate	0.1-1%
	Phenolphthalein	<0.1%
	HFC 134a (liquated gas)	5-20%
	Water (as required for)	100%
10	Where the percentages are percentages in weight and	t relative to the total descaling composition;

# B) a fixative containing:

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NaOH	5-15%
sepiolite	2-8%
sodium dodecylsulphate	0.1-1%
HFC 134a (liquated gas)	5-20%
Water (as required for)	100%
Where the percentages are percentages in weight rela	tive to the total fixative composi-
tion.	

- 34. Cleaning product according to Claim 1, in which the descaling composition is presented as foam, spray gel or gel.
  - 35. Cleaning product according to Claim 1, in which the fixative is present as foam or spray gel.

36. A method for cleaning titanium surfaces that refers to the application of a cleaning product according to any of Claims 1 to 35. 37. Method according to Claim 36 that includes the following stages: 5 a) application of the descaling substance of the said cleaning product on the surface to be cleaned and leaving this to act for a given period of time; b) application of the fixative of this cleaning product to the titanium surface previously treated with this descaling substance in stage a), and leaving this to act for a given period of time; 10 c) aspiration of the titanium surface previously treated with these descaling and fixative substances in stages a) and b); and 15 d) rinsing the treated titanium surface after carrying out stage c). 38. Method according to Claim 37, in which the application of this descaling substance to the titanium surface to be cleaned is done by a spray gun or by a sponge trowel, and left to act for a period of time ranging from 15 seconds to 10 minutes before applying the fixative. 20 39. Method according to Claim 37, in which the application of this fixative on the titanium surface to be cleaned, previously treated with the descaling substance is done using a spray gun, and is left to act for a period ranging from 15 seconds to 5 minutes before starting stage c) after confirming that the neutralization has taken place. 25 40. Method according to Claim 37, in which rinsing of the treated titanium surface is done with water jets at a temperature ranging from 5°C to 30°C. 30 35 40 45 50 55

# INTERNATIONAL SEARCH REPORT International application No. PCT/ ES 01/00401 CLASSIFICATION OF SUBJECT MATTER C23G 1/02; C23F 1/16; 3/06 According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C23G; C23F Documentation scarched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI, EPODÓC C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Category\* Relevant to claim No. WO 0100906 A [ORGANISATION EUROPEENNE POUR LA RECHERCHE NUCLEAIRE (CERN)] 04.01.2001. A Α EP 1029953 A (AEROSPATIALES MATRA) 23.08.2000. A US 5217569 A (HENRY M.Hodgens II et al) 08.06.1993. A US 3844859 A (WINBERG, RAGNAR) 29.10.1974. X See patent family annex. Further documents are listed in the continuation of Box C. later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 10 May 2002 (10.05.02) 21 May 2002 (21.05.02) Name and mailing address of the ISA/ Authorized officer S.P.T.O. Facsimile No. Telephone No.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/ ES 01/00401

Patent document cited in search report	Publication date	Patent familiy member(s)	Publication date
WO 0100906 A	04.01.2001	FR 2795433 AB	29.12.2000
		AU 6449700 A	31.01.200
		EO 1194617 A	10.04.2002
		***************************************	
EP 1029953 A	23.08.2000	FR 2789408 AB	11.08.2000
	••	JP 2000239894 A	05.09.2000
		US 6258242 B	10.07.2001
US 5217569 A	08.06.1993	US 5102499 A	07.04.1992
US 3844859 A	29.10.1974	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)